



# Boosting photoelectrocatalytic oxygen evolution activity of BiVO<sub>4</sub> photoanodes via caffeic acid bridged to NiFeOOH

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## ABSTRACT

Bismuth vanadate (BiVO<sub>4</sub>) is a promising n-type photoanode material for photoelectrochemical (PEC) water splitting. However, its activity is impeded by poor charge carrier transport and sluggish oxygen evolution kinetics. In this study, we reports a Fe doping and caffeic acid (CA)/NiFeOOH (NiFe) modification with BiVO<sub>4</sub> photoanode (NiFe/CA/Fe-BiVO<sub>4</sub>) to enhance the PEC water oxidation performance and stability. The modified BiVO<sub>4</sub> demonstrates significant advantages in promoting the PEC performance and stability. Specifically, Fe doping via in-situ electro-deposition results in smaller crystal sizes, larger specific surface areas, and more exposed active sites. Furthermore, co-catalyst NiFe connects with Fe-BiVO<sub>4</sub> through CA bridge facilitates a more uniform self-assembly distribution of NiFe on BiVO<sub>4</sub> surface. The NiFe/CA/Fe-BiVO<sub>4</sub> exhibits an excellent photocurrent density of 6.2 mA/cm<sup>2</sup> at 1.23 V<sub>RHE</sub> and demonstrates good stability at 0.8 V<sub>RHE</sub>. In addition, the composite photoanode shows a high applied bias photon-to-current efficiency (ABPE) value of 2.15% at 0.65 V<sub>RHE</sub>. EPR and in-situ FTIR confirm the generation of superoxide active species (O<sub>2</sub><sup>•−</sup> and ·O<sub>2</sub>) during the PEC water oxidation reaction.

## 1. Introduction

Converting solar energy into clean hydrogen fuels via photoelectrochemical (PEC) water splitting has been considered as a highly promising and effective strategy [1–3]. Due to the narrow bandgap (2.4 eV) and suitable energy-band position [4,5], BiVO<sub>4</sub> is regarded as a highly potential photoanode material for overcoming the slow water oxidation half-reaction (OER) kinetics [6,7]. However, the easy recombination of charge carriers in BiVO<sub>4</sub> and its slow surface dynamics result in the majority of photo-generated carriers recombining in the bulk and at the surface, which hinder BiVO<sub>4</sub> from reaching its theoretical maximum photocurrent density (7.5 mA/cm<sup>2</sup>, AM 1.5 G, 100 mW/cm<sup>2</sup>) at 1.23 V<sub>RHE</sub> [8–10]. Meanwhile, V<sup>5+</sup> dissolution from the crystal under illumination causes the photocurrent of the BiVO<sub>4</sub> photoanode to drop significantly within a short period of time [11]. Therefore, it is crucial for BiVO<sub>4</sub> to enhance the PEC performance and

improve the long-time stability. Various strategies, such as morphology engineering [12,13], elemental doping [14–16], surface facet control [17–19], constructing heterojunctions [20], loading hole-transporting layers [21,22] and loading co-catalysts [23,24] have been developed, which are able to efficiently promote carrier separation and transport in the bulk phase and on the surface as well as to significantly improve the stability of BiVO<sub>4</sub>.

The photocurrent density is significantly improved by doping BiVO<sub>4</sub> with heteroatom such as Mo, W, P, N and F [20,25–29]. In the past decade, transition metal oxides and hydroxides (such as FeOOH, NiOOH, NiOOH/FeOOH, NiFeOOH (NiFe), N:NiFeO<sub>x</sub> and FeNiPO<sub>x</sub>) on BiVO<sub>4</sub> as oxygen evolution co-catalysts (OEC) has been widely applied to enhance its PEC performance and stability [4,8,24,30–32]. Furthermore, some solution treatment methods have also been shown to significantly improve the PEC performance and stability of BiVO<sub>4</sub> [9,11,31,33]. For example, long-term photo-assisted electrochemical

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passivation of the  $\text{BiVO}_4$  surface can greatly enhance its PEC performance and stability [33]. Simultaneously, the addition of  $\text{V}^{5+}$  to the reaction solution can effectively improve the stability of  $\text{BiVO}_4$  [11]. Although there have been many reports to enhance the PEC performance of  $\text{BiVO}_4$  via doping heteroatom, these methods are relatively expensive, and the study of interface relationships is still unclear.

Herein we reported a method for preparing a layer-by-layer structure  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode via doping in-situ electrochemical deposition process and with coffee acid (CA) as a coordinating-assisted impregnation agent. During the rapid formation of  $\text{BiOI}$  in electrodeposition, Fe is encapsulated into the lattice as a heteroatom. Experimental and characterization results demonstrated that the Fe was uniformly distributed in  $\text{BiVO}_4$ , which improved the transport of photogenerated charge carriers at the bulk and surface, generated more oxygen vacancies, suppressed carrier recombination and enhanced water oxidation performance. Subsequently, coffee acid acted as a bridging agent to connect  $\text{Fe-BiVO}_4$  and  $\text{NiFe}$ . Carboxyl groups at the end of coffee acid coordinated with Ni and Fe atoms, forming a uniform  $\text{NiFeOOH}$  outer layer during the impregnation process, which ultimately resulted in the layer-by-layer structure of  $\text{NiFe/CA/Fe-BiVO}_4$ . This coordination-driven self-assembly process not only formed stable bonds for fast charge transfer but also provided a clear interface for structural-activity studies.

## 2. Materials and methods

The specific reagents, equipment, experimental procedures and analytical methods employed in this study are detailed in the [Supporting Information](#).

## 3. Results and discussion

### 3.1. Construction of $\text{NiFe/CA/Fe-BiVO}_4$ Photoanode

$\text{M-BiVO}_4$  ( $\text{M} = \text{Fe, Co, Ni, Mn}$  and  $\text{Zn}$ ) was obtained based on a reported method with modification [8], which was prepared through doping in electrodeposition process and then high-temperature calcination. The doping elements and doping amounts had a significant impact on the performance of the photoanode. Different doping amounts of  $\text{M-BiVO}_4$  were prepared by adding varying amounts of different chloride salts to the electrolyte. Among the five types of photoanodes doped with different heteroatoms, namely  $\text{Fe-BiVO}_4$ ,  $\text{Co-BiVO}_4$ ,  $\text{Zn-BiVO}_4$ ,  $\text{Ni-BiVO}_4$  and  $\text{Mn-BiVO}_4$ , the 0.5- $\text{Fe-BiVO}_4$  photoanode exhibit the highest photocurrent density, approximately  $4.20 \text{ mA/cm}^2$  at  $1.23 \text{ V}_{\text{RHE}}$  (Fig. S1). The elemental content of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$  are determined by inductively coupled plasma optical emission spectra (ICP-OES) (Table S1). Therefore, it was selected for subsequent studies.

After optimization doping concentrations, samples  $\text{Ni-BiVO}_4$ ,  $\text{Co-BiVO}_4$ ,  $\text{Mn-BiVO}_4$  and  $\text{Zn-BiVO}_4$  show the maximum photocurrent densities of 4.00, 3.90, 3.02 and  $3.01 \text{ mA/cm}^2$ , respectively.

Scanning electron microscopy (SEM) is used for characterizing the morphology of photoanodes.  $\text{BiVO}_4$  is uniformly grown on FTO with 200–400 nm porous nanostructure (Fig. 2a). This structure is beneficial for enhancing the catalyst's light absorption, accelerating reactants diffusion and exposing more active sites. And  $\text{Fe-BiVO}_4$  (Fig. 2b) exhibits a similar morphology to  $\text{BiVO}_4$ . However, the nanoparticles of  $\text{Fe-BiVO}_4$  are smaller than those of  $\text{BiVO}_4$ , indicating that Fe doping alters the particle size of  $\text{BiVO}_4$  and exposes more active sites. Fe doping takes place during the electrodeposition process of  $\text{BiOI}$  (Fig. 1). The presence of  $\text{FeCl}_3$  in the solution results in a more negative current (Fig. S2). A more negative current will consume more  $\text{H}^+$ , resulting in a more drastic change in pH near FTO [34], thus accelerating the crystallization process of  $\text{BiOI}$  and shortening the time required for crystallization. The faster crystallization process and shorter crystallization time results in the formation of smaller crystals. Because the particle size of  $\text{BiOI}$  decreased, crystal size of  $\text{Fe-BiVO}_4$  became smaller than that of pure  $\text{BiVO}_4$ . Subsequently, through the method of caffeic acid bridging and impregnation self-assembly,  $\text{NiFeOOH}$  co-catalyst was successfully constructed on  $\text{Fe-BiVO}_4$ , resulting in the preparation of a  $\text{NiFe/CA/Fe-BiVO}_4$  composite photoanode. It can be observed that the surface of  $\text{Fe-BiVO}_4$  becomes noticeably rougher after loading  $\text{NiFe/CA}$  (Fig. 2c).

The transmission electron microscopy (TEM) spectra of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$  are shown in Fig. S3, S4 and 1d. Compared to  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ ,  $\text{NiFe/CA/Fe-BiVO}_4$  clearly exhibits a uniform outer layer of  $\text{NiFe}$  co-catalyst. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 2e) also confirms the presence of the  $\text{NiFe}$  layer. In  $\text{NiFe/CA/Fe-BiVO}_4$ , there is a  $\text{NiFe}$  film with a thickness of approximate 5 nm on the surface of  $\text{Fe-BiVO}_4$ , and the interface between  $\text{Fe-BiVO}_4$  and the  $\text{NiFe}$  layer is indicated by a yellow dashed line. The lattice fringe with a width of 0.237 nm corresponds to the (220) crystal plane of  $\text{BiVO}_4$ . The homogeneous dispersion of Bi, V, O, Fe and Ni elements in samples are confirmed by the elemental mapping of  $\text{NiFe/CA/Fe-BiVO}_4$  (Fig. 2g).

Additionally, crystal phase and crystallinity degree of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$  samples are verified by the X-ray diffraction (XRD) patterns (Fig. 2f). It can be observed that all the diffraction peaks are attributed to monoclinic  $\text{BiVO}_4$  (JCPDS No. 14–0688), suggesting that the doping does not alter the phase and crystallinity of  $\text{BiVO}_4$ . However, no obvious diffraction peaks corresponding to  $\text{NiFeOOH}$  are detected in the XRD pattern, which is mainly due to its amorphous structure and ultra-thin thickness. Furthermore, the XRD patterns of other  $\text{M-BiVO}_4$  ( $\text{M} = \text{Co, Ni, Zn}$  and  $\text{Mn}$ ) are similar to  $\text{BiVO}_4$  (Fig. S5a), demonstrating the universality of this electrochemical in-situ doping approach. The XRD pattern of  $\text{NiFe/Fe-BiVO}_4$

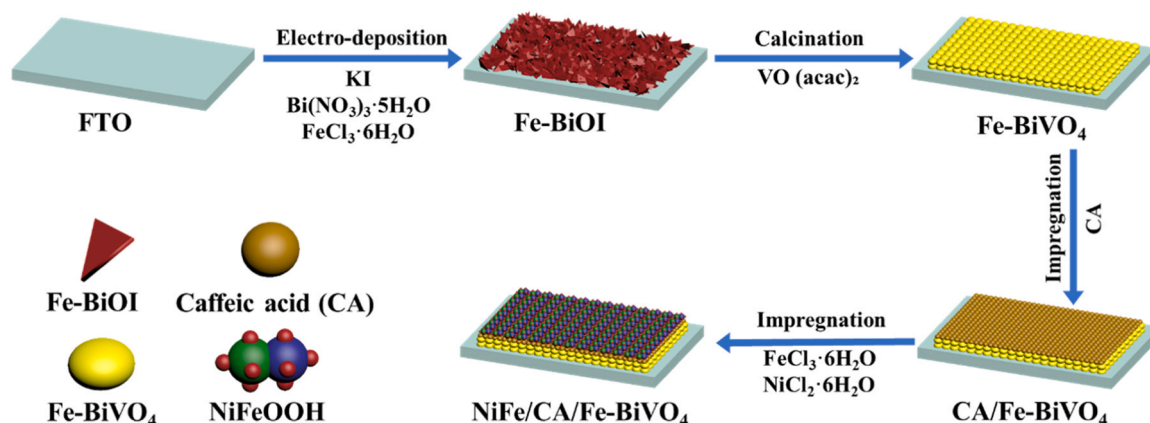
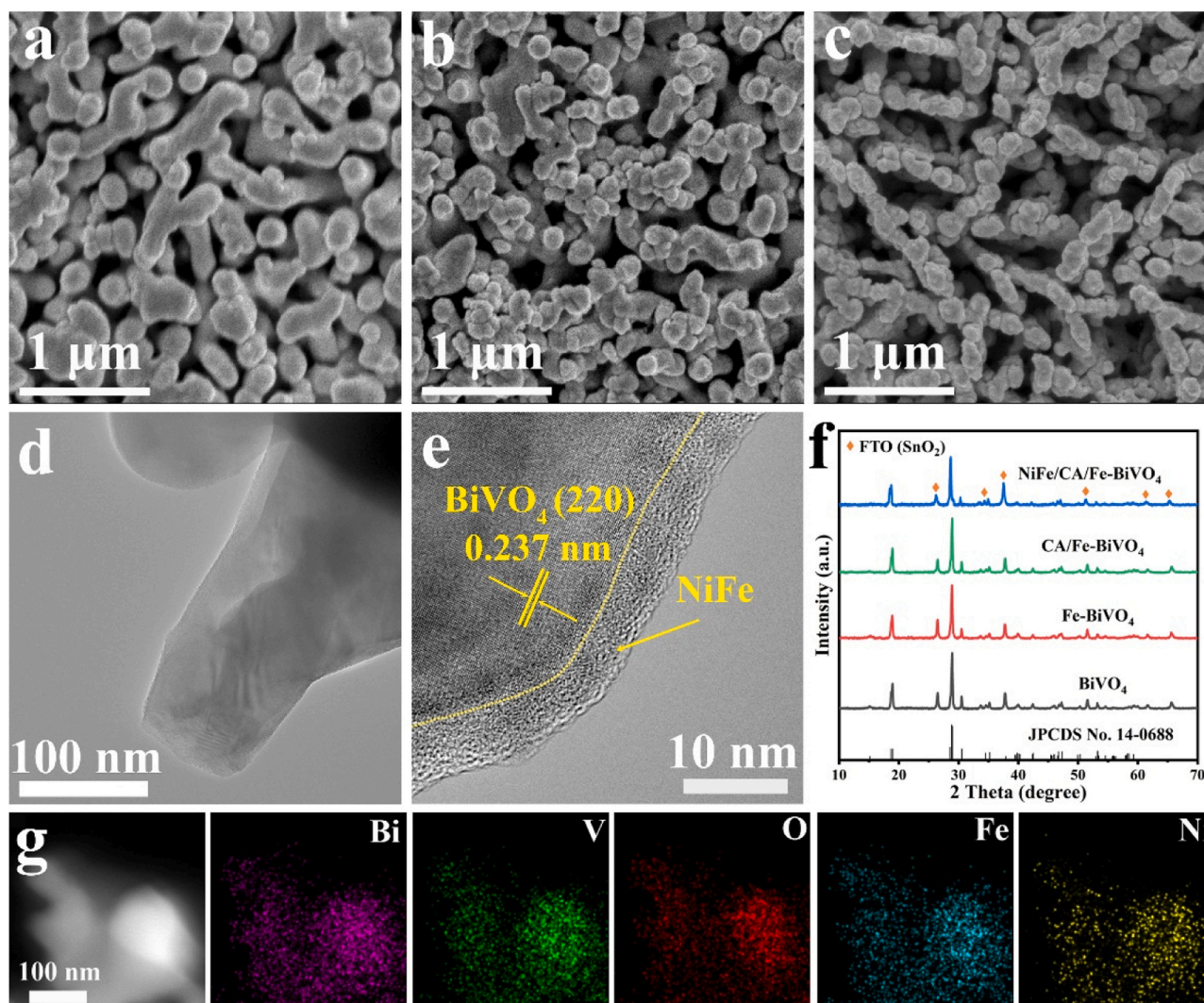


Fig. 1. Schematic illustration for synthesizing  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode.



**Fig. 2.** Characterization of morphology and crystal phase. a), b) and c) SEM images of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . d) TEM and e) HRTEM images of  $\text{NiFe/CA/Fe-BiVO}_4$ . f) XRD spectra of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . g) Elemental mapping images of Bi, V, O, Fe and Ni of the  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode.

(Fig. S5b) also exhibits no obvious differences with  $\text{NiFe/CA/Fe-BiVO}_4$ , revealing that the presence of CA has no effect on the crystal phase and crystallinity of the composite photoanode.

Fourier-transform infrared spectroscopy (FTIR) was used to demonstrate the successful anchoring of CA onto  $\text{BiVO}_4$  (Fig. 3a). For pure CA, the band at  $1670\text{ cm}^{-1}$  is due to the absorption of  $\text{C=O}$ , while the band at  $950\text{ cm}^{-1}$  and the weaker bands at  $3200\text{--}3500\text{ cm}^{-1}$  are attributed to the out-of-plane bending vibration of the carboxyl group O-H and the outward bending vibration of adjacent hydroxyl groups, respectively [35]. The double bands at around  $2800\text{ cm}^{-1}$  are attributed to the stretching vibration of the C-H bond, which confirms the successful anchoring of CA onto  $\text{Fe-BiVO}_4$  and the bridging of  $\text{NiFeOOH}$ . The solid-state UV-vis spectra of four samples exhibit very similar absorption range (Fig. S6a). Band gap ( $E_g$ ) values of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$  catalysts are 2.39 eV and 2.36 eV (Fig. 3b), respectively, through Kubelka-Munk transformation [36].

The Mott-Schottky can be used to determine the conduction band position ( $E_{CB}$ ) of semiconductors. Both curves of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$  show positive slopes (Fig. 3c and 3d), suggesting that they are n-type semiconductors [37]. The flat band potentials are 0.18 eV and 0.22 eV for  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ , respectively, and the corresponding  $E_c$  positions are  $-0.02\text{ eV}$  and  $0.02\text{ eV}$ . The valence band position ( $E_{VB}$ ) of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$  are 2.37 eV and 2.38 eV, respectively, which is

calculated from formula  $E_{VB} = E_{CB} + E_g$ . Fe doping alters the band structure of  $\text{BiVO}_4$  and enhances oxidation capability of  $\text{Fe-BiVO}_4$ . Furthermore, under the same conditions, the Mott-Schottky curve of  $\text{Fe-BiVO}_4$  has a gentler slope compared to  $\text{BiVO}_4$ , indicating a higher concentration of charge carriers in the composite  $\text{Fe-BiVO}_4$  photoanode [37]. This allows for greater extraction of holes from the bulk phase for interfacial reactions, thereby accelerating the separation and transport of photogenerated charge carriers in the bulk phase [37–39].

### 3.2. Photoelectrochemical performance

All photoelectrochemical tests of the photoanodes were conducted in a 0.5 M borate buffer solution with a three-electrode system ( $\text{pH} = 9.5$ , AM 1.5 G,  $100\text{ mV/cm}^2$ ). The photocurrent densities of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{NiFe/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$  at  $1.23\text{ V}_{\text{RHE}}$  are 1.5, 4.2, 5.1 and  $6.2\text{ mA/cm}^2$  (Fig. 4a and S8a), respectively. The relatively poor PEC performance of pure  $\text{BiVO}_4$  is mainly attributed to the slow water oxidation kinetics on the surface of  $\text{BiVO}_4$  and the recombination of photogenerated charge carriers. Whereas, when Fe was doped in the  $\text{BiVO}_4$ , the photocurrent density increases to  $4.2\text{ mA/cm}^2$  for  $\text{Fe-BiVO}_4$  at the same voltage. The reason is that more holes are extracted from the bulk phase for surface reactions, thus accelerating the separation and transport of photogenerated charge carriers in the bulk phase and



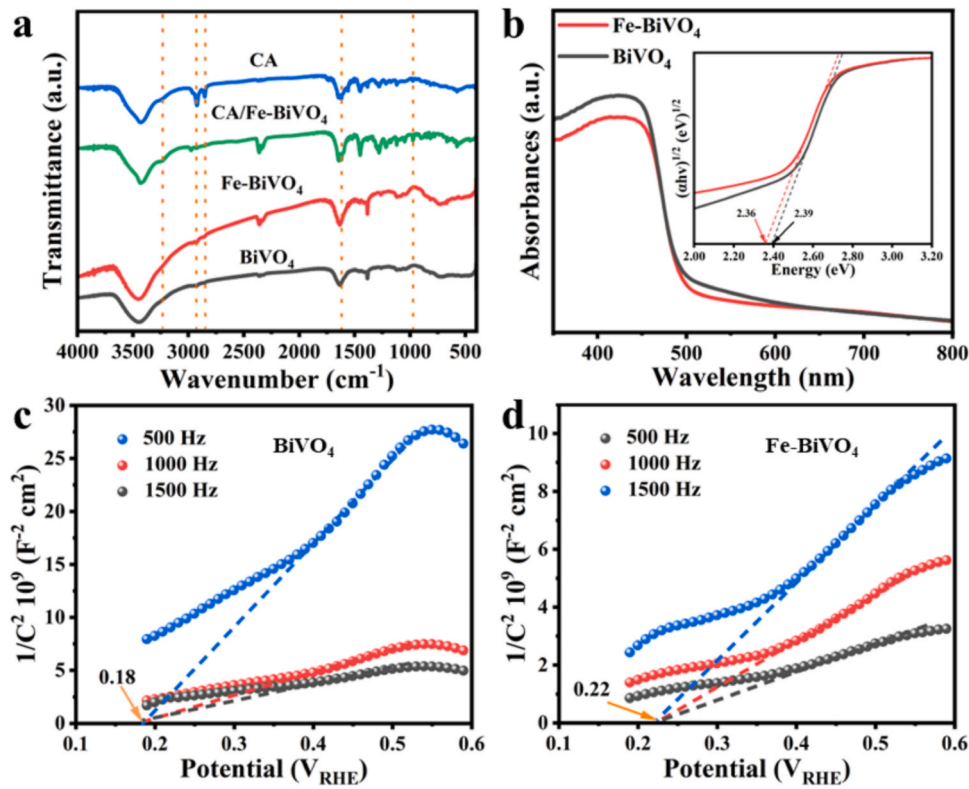


Fig. 3. a) FTIR spectra of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{CA}$ . b) Bandgap calculation diagrams of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ . The Mott-Schottky curves of c)  $\text{BiVO}_4$  and d)  $\text{Fe-BiVO}_4$ .

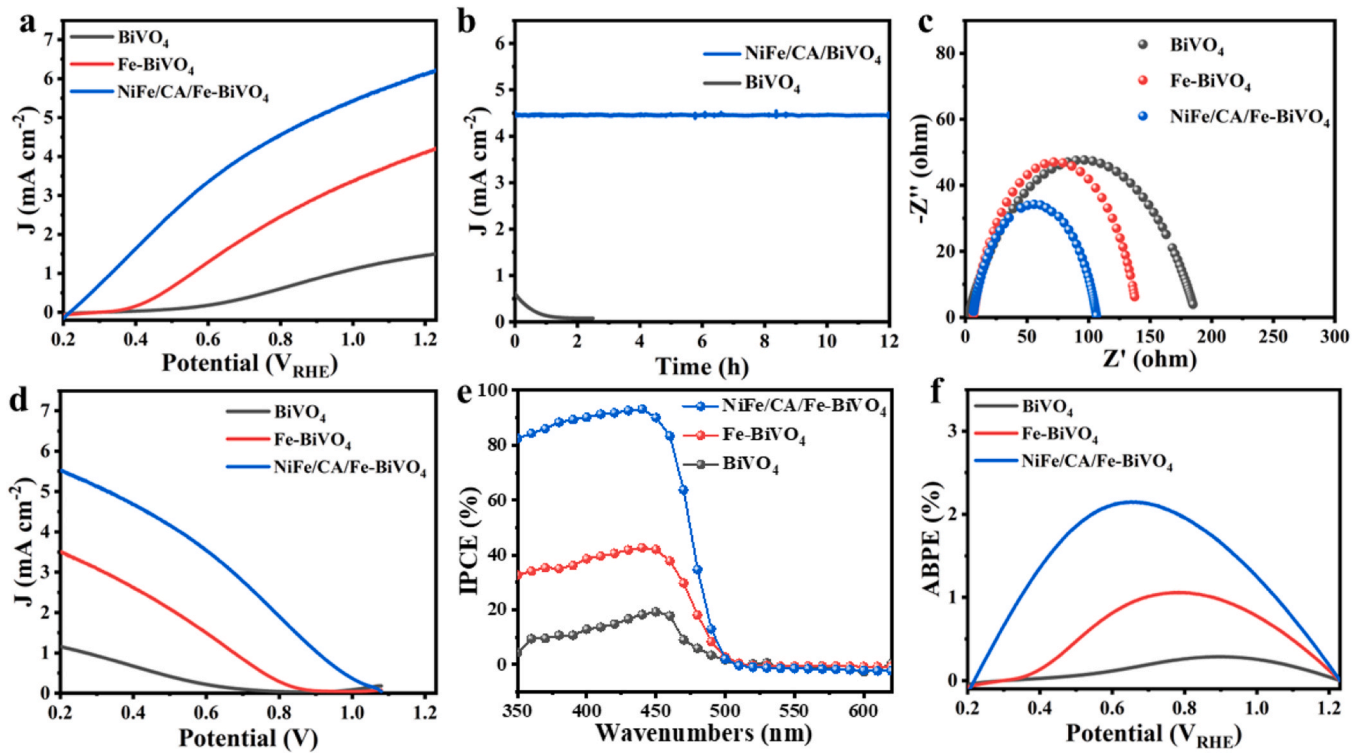


Fig. 4. PEC performance of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . a)  $J$ - $V$  curves. b)  $i$ - $t$  curves of  $\text{BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$  at 0.8  $V_{\text{RHE}}$ . c) EIS curves. d) Photovoltaic characteristic. e) IPCE curves. f) ABPE curves.



surface. When the Fe-BiVO<sub>4</sub> surface was further modified with a NiFe/CA co-catalyst, the NiFe/CA/Fe-BiVO<sub>4</sub> photoanode exhibits the highest photocurrent density of 6.2 mA/cm<sup>2</sup> at 1.23 V<sub>RHE</sub> and more negative onset potential shift, demonstrating excellent PEC performance. NiFe/CA co-catalyst decreases the surface states of BiVO<sub>4</sub> and promotes the transfer of photogenerated carriers between the solid-liquid interfaces.

Stability of photoanode is an important factor to evaluate potential actual application. In addition to its outstanding photoelectrochemical conversion efficiency, the NiFe/CA/Fe-BiVO<sub>4</sub> photoanode also shows improved stability. The photocurrent density of BiVO<sub>4</sub> quickly decays to a very low value under an applied voltage of 0.8 V<sub>RHE</sub> (Fig. 4b), indicating stability of BiVO<sub>4</sub> is very poor [40]. This is caused by the dissolution of V<sup>5+</sup> from the BiVO<sub>4</sub> crystal into the electrolyte [11,32,40,41]. At high applied bias potential, more accumulated holes causes corresponding changes on the local structure of the BiVO<sub>4</sub>, thus destroying the stability of the BiVO<sub>4</sub> lattice and increasing the dissolution of V<sup>5+</sup> on the BiVO<sub>4</sub> surface [11]. However, when strategies of iron doping and NiFe/CA as co-catalyst were adopted, even after 12 hours, the photocurrent density of the NiFe/CA/Fe-BiVO<sub>4</sub> photoanode remains close to its initial value. The presence of the NiFe/CA layer effectively prevents the dissolution of V<sup>5+</sup> from the BiVO<sub>4</sub> photoanode and maintains the stability of the crystal structure.

In order to make clear the interfacial charge transfer and oxygen evolution kinetic, electrochemical impedance spectroscopy (EIS) was measured. The EIS of the photoanodes (Fig. 4c) follows the order of BiVO<sub>4</sub> > Fe-BiVO<sub>4</sub> > NiFe/CA/Fe-BiVO<sub>4</sub>. The photoelectric characteristics of the photoanodes can be obtained by subtracting the PEC performance of the photoelectrode from its corresponding electrochemical performance (Fig. 4d). The open-circuit voltage of BiVO<sub>4</sub> is only 0.7 V. After doping with Fe, the open-circuit voltage of Fe-BiVO<sub>4</sub> increases to about 0.85 V. When NiFe/CA layer was further loaded, the open-circuit voltage reaches approximately 1.15 V with short-circuit current density.

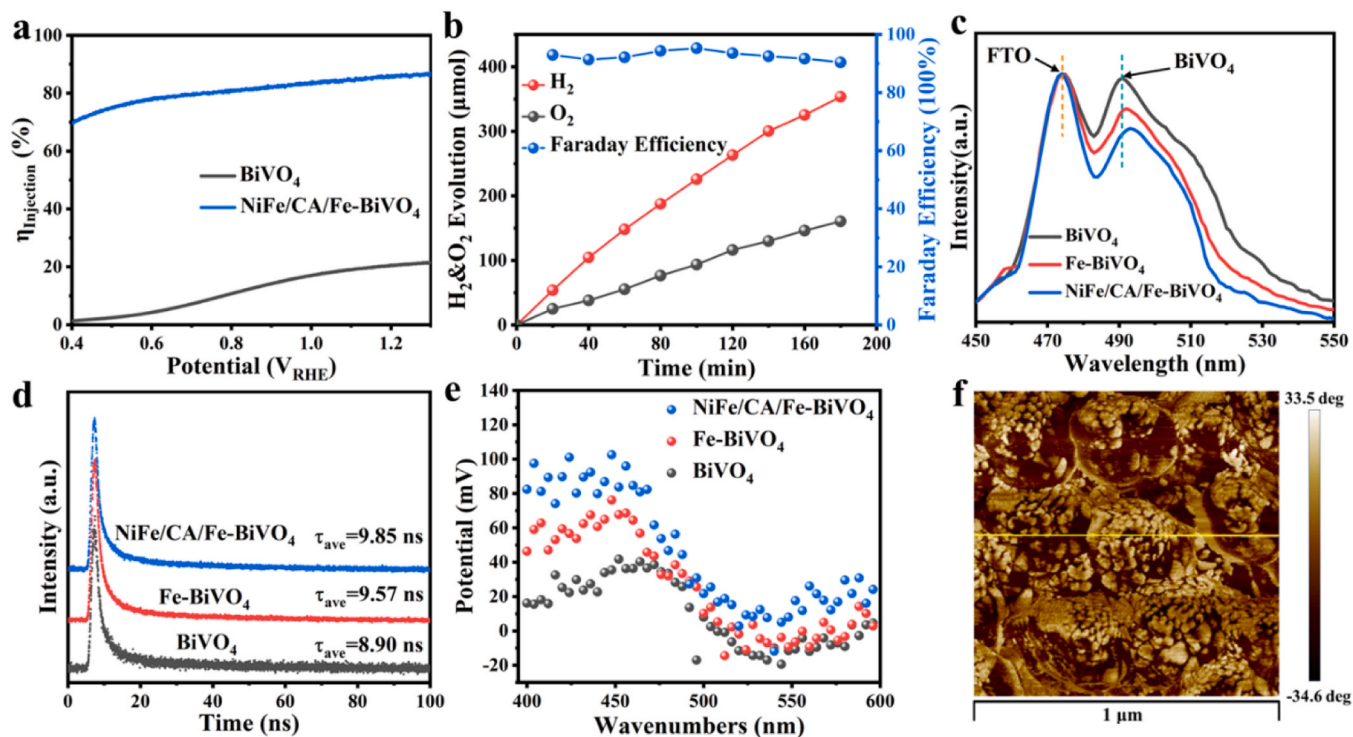
To investigate the photogenerated carrier dynamics of oxygen evolution, the incident photon-to-current conversion efficiency (IPCE) values of the photoanodes were tested at 1.23 V<sub>RHE</sub> in borate buffer.

NiFe/CA/Fe-BiVO<sub>4</sub> exhibits a 93% IPCE value, which is much higher than BiVO<sub>4</sub> (19%) and Fe-BiVO<sub>4</sub> (42%, Fig. 4e), indicating that doping Fe and NiFe/CA co-catalyst layer improve the photon-to-current conversion efficiency of the photoanode. NiFe/CA/Fe-BiVO<sub>4</sub> shows the highest the applied bias photon-to-current efficiency (ABPE) value of 2.15% at 0.65 V<sub>RHE</sub>, which is much higher than that of Fe-BiVO<sub>4</sub> (1.06% at 0.80 V<sub>RHE</sub>) and pristine BiVO<sub>4</sub> (0.29% at 0.90 V<sub>RHE</sub>, Fig. 4f), respectively. These studies demonstrate that the NiFe/CA co-catalyst layer not only significantly improves the PEC performance of the BiVO<sub>4</sub> photoanode but also enhances its stability.

### 3.3. Spectra and electrochemical analysis

To clarify the interface natures on PEC performance, the charge injection efficiency ( $\eta_{\text{injection}}$ ) and charge separation efficiency ( $\eta_{\text{separation}}$ ) of BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub> were evaluated in borate buffer containing Na<sub>2</sub>SO<sub>3</sub> as a hole scavenger. The  $\eta_{\text{separation}}$  of BiVO<sub>4</sub> is only slightly lower than that of NiFe/CA/Fe-BiVO<sub>4</sub> (Fig. S10). But based on J–V curves (Fig. S8b), the NiFe/CA/Fe-BiVO<sub>4</sub> exhibits a much higher charge injection efficiency ( $\eta_{\text{injection}}$ ) (86.1%) compared with that of BiVO<sub>4</sub> (20.8%, Fig. 5a) at 1.23 V<sub>RHE</sub>. The NiFe/CA co-catalyst layer significantly contributes to improving charge separation and hole transport at the catalyst-solution interface, and greatly accelerates the surface catalytic reaction rate. After 3 h reaction, the evolution amount of H<sub>2</sub> and O<sub>2</sub> is 353.6  $\mu$ mol and 160.5  $\mu$ mol respectively, with an average Faradaic efficiency of 92% (Fig. 5b). This further proves the excellent water oxidation capability of the NiFe/CA/Fe-BiVO<sub>4</sub>, which illustrates that the presence of CA is beneficial to the water oxidation reaction occurring on the surface of the NiFe layer.

Charge separation capability was explored in depth by steady-state photoluminescence (PL) spectroscopy. The peak at 473 nm corresponds to the characteristic peak of FTO conductive glass (Fig. 5c). The peak at the wavelength of 490 nm is near the UV–vis absorption edge of BiVO<sub>4</sub>, which represents the characteristic absorption peak of BiVO<sub>4</sub> [24, 42,43]. The appearance of this peak is due to the radiative



**Fig. 5.** Spectra and electrochemical analysis. a) Charge injection efficiency curves of BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub>. b) H<sub>2</sub> and O<sub>2</sub> evolution of NiFe/CA/Fe-BiVO<sub>4</sub>. c) PL spectra and d) TR-PL spectra of BiVO<sub>4</sub>, Fe-BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub>. e) SPV spectra of BiVO<sub>4</sub>, Fe-BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub>. f) 2D KPFM spectra of NiFe/CA/Fe-BiVO<sub>4</sub>.

recombination of the electrons in V 3d conduction band (CB) and the holes in Bi 6s and O 2p valence band (VB). The PL peak intensity represent the recombination ability of photogenerated carriers. BiVO<sub>4</sub> photoanode exhibits the strongest PL peak, indicating it has the highest electron-hole recombination ability. However, after doping with Fe and loading with NiFe/CA co-catalyst, the intensity of the PL peak gradually decreases. Fe doping and NiFe/CA co-catalyst both enhance charge separation ability of BiVO<sub>4</sub> photoanode and NiFe/CA/Fe-BiVO<sub>4</sub> gives the strongest charge separation ability. In addition, the PL characteristic peak of Fe-BiVO<sub>4</sub> red shift occurs, which is caused by the narrowing of its bandgap due to Fe doping and oxygen vacancies.

The time-resolved photoluminescence (TR-PL) spectroscopy is used to probe the decay kinetic of photogenerated carrier lifetimes. The average lifetimes of the photogenerated carriers for the BiVO<sub>4</sub>, Fe-BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub> photoanodes increase successively as 8.90, 9.57 and 9.85 ns (Fig. 5d), fitting parameters shown in Table S2. The tendency is consistent with the photocurrent density and more photogenerated carriers participate in surface reactions. Compared with BiVO<sub>4</sub>, the longer photogenerated carrier lifetime of Fe-BiVO<sub>4</sub> disclose doping Fe enhanced charge separation ability. As for NiFe/CA/Fe-BiVO<sub>4</sub>, the photogenerated carriers transfer from Fe-BiVO<sub>4</sub> to the NiFe/CA co-catalyst layer, leading to an increase of the photogenerated carrier lifetime. Therefore, NiFe/CA/Fe-BiVO<sub>4</sub> demonstrates the lowest recombination rate of photogenerated carriers, resulting in more photogenerated holes participate in the surface water oxidation.

To further investigate the surface photovoltaic properties, surface photovoltage (SPV) tests were conducted using a Kelvin probe force microscope (KPFM) under illumination. BiVO<sub>4</sub>, Fe-BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub> all exhibit positive surface photovoltage (Fig. 5e) when they were excited by light with the same wavelength, which is attributed to the enrichment of photogenerated holes at the surface[44]. The surface photovoltage of NiFe/CA/Fe-BiVO<sub>4</sub> is greatly higher than that of Fe-BiVO<sub>4</sub> and BiVO<sub>4</sub>, with the differences of approximately 40 mV and 80 mV under 400 nm excitation, respectively. The pronounced surface potential difference elucidates a greater accumulation of photogenerated holes on the NiFe surface in the NiFe/CA/Fe-BiVO<sub>4</sub> composite photoanode, while the photogenerated electrons gather in Fe-BiVO<sub>4</sub>. Furthermore, there exists a strong built-in electric field and efficient charge separation between the NiFe/CA co-catalyst and Fe-BiVO<sub>4</sub> photoanode. The two- and three-dimensional images of NiFe/CA/Fe-BiVO<sub>4</sub> (Fig. 5f and S11) obtained from KPFM during the SPV testing show the same morphology as its SEM image (Fig. 2c). Fig. S12 represents the surface roughness analysis at the position indicated by the yellow line in Fig. 5f.

### 3.4. Active species and electronic states

In order to further confirm the active species during the reaction

process over NiFe/CA/Fe-BiVO<sub>4</sub>, electron paramagnetic spectroscopy (EPR) and in-situ Fourier transform infrared (in-situ FTIR) tests were conducted to detect the solution of water oxidation reaction. The generation of superoxide active species  $\cdot\text{O}_2^-$  during the reaction is verified by the characteristic signal of EPR (Fig. 6a)[45,46]. In the in-situ FTIR spectra, the bands at 1059 and 1160  $\text{cm}^{-1}$  become enhanced with increasing reaction time (Fig. 6b), which are assigned as of  $\text{O}_2^{\cdot-}$  and  $\text{OOH}^{\cdot}$  active species[47]. EPR and in-situ FTIR tests disclose that the water molecules adsorbed on the electrode surface are first dissociated into OOH through photogenerated holes on the Fe and Ni active sites under illumination conditions. Then they are transformed into superoxide species ( $\text{O}_2$  and  $\cdot\text{O}_2^-$ ) intermediates, and further converted into oxygen molecules, which finally are released from the NiFe/CA/Fe-BiVO<sub>4</sub> photoanode surface.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical states of the photoanode and the electronic states of its elements. Compared with pure BiVO<sub>4</sub>, upon doping Fe, the peaks of Bi 4f, V 2p and O 1s in Fe-BiVO<sub>4</sub> shift towards lower binding energies (Fig. 7a-c), indicating an increase in electron cloud density around Bi, V and O atoms due to the formation of oxygen vacancies[2,26,48]. When CA was anchored to Fe-BiVO<sub>4</sub> through coordination, the peaks of Bi 4f, V 2p and O 1s in CA/Fe-BiVO<sub>4</sub> shift towards higher binding energies, suggesting a strong interaction between CA and Fe-BiVO<sub>4</sub>. Subsequently, with the growth of the NiFe co-catalyst layer on CA/Fe-BiVO<sub>4</sub>, the peaks of Bi 4f, V 2p and O 1s in NiFe/CA/Fe-BiVO<sub>4</sub> shift towards lower binding energies, revealing electron transfer from Fe, Ni to Bi, V atoms [41]. Fe doping and NiFe modification cause the V peak in NiFe/CA/Fe-BiVO<sub>4</sub> to shift towards lower binding energies, which increases the electron cloud density around V atoms, effectively suppressing the dissolution of  $\text{V}^{5+}$  [32,41] and enhancing the stability of the photoanode (Fig. 7b).

The XPS characteristic peaks of BiVO<sub>4</sub> located at 529.9 eV, 531.0 eV and 531.9 eV are attributed to lattice oxygen ( $\text{O}_\text{L}$ ), oxygen vacancies ( $\text{O}_\text{V}$ ), and adsorbed oxygen ( $\text{O}_{\text{OH}}$ ), respectively [49,50] (Fig. 7c and 7d). After doping, the quantity of  $\text{O}_\text{V}$  in Fe-BiVO<sub>4</sub> increases compared to pure BiVO<sub>4</sub>, indicating the generation of a certain number of oxygen vacancies. However, when CA was loaded, the quantity of  $\text{O}_\text{V}$  decreases, which is attributed to the anchoring of -OH groups from CA to the oxygen vacancies on the surface of Fe-BiVO<sub>4</sub>. In the composite photoanode NiFe/CA/Fe-BiVO<sub>4</sub>, both the content of  $\text{O}_\text{V}$  and  $\text{O}_{\text{OH}}$  obviously increase, indicating that the NiFe co-catalyst prepared by the impregnation method contains a large number of  $\text{O}_\text{V}$  and  $\text{O}_{\text{OH}}$  and the NiFe/CA/Fe-BiVO<sub>4</sub> photoanode has better adsorption capacity for water molecules [51,52].

The peaks of Fe 2p<sub>1/2</sub> (723.9 eV) and Fe 2p<sub>3/2</sub> (710.9 eV) are attributed to  $\text{Fe}^{2+}$ , while the peaks of Fe 2p<sub>1/2</sub> (726.4 eV) and Fe 2p<sub>3/2</sub> (713.0 eV) are attributed to  $\text{Fe}^{3+}$  (Fig. 7e) [32,50,53]. The peaks of Ni 2p<sub>3/2</sub> (873.5 eV) and Ni 2p<sub>1/2</sub> (855.9 eV) with satellite signals are

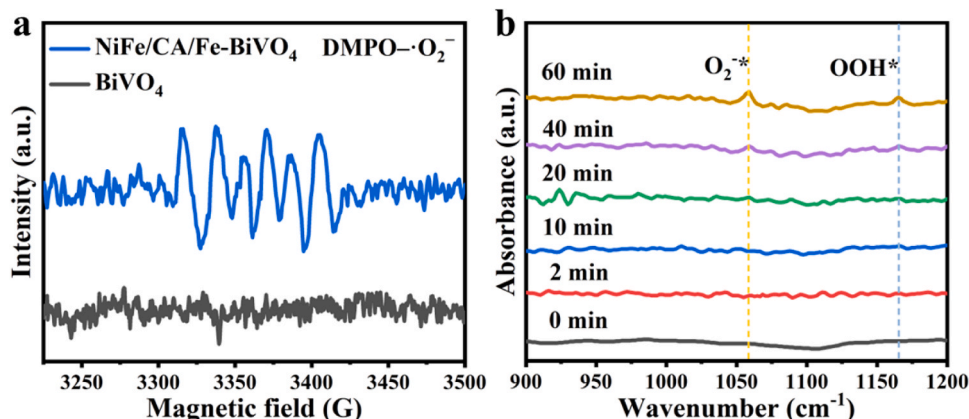


Fig. 6. a) EPR spectra of DMPO- $\cdot\text{O}_2^-$  in BiVO<sub>4</sub> and NiFe/CA/Fe-BiVO<sub>4</sub> reaction solutions, and b) In-situ FTIR spectra of NiFe/CA/Fe-BiVO<sub>4</sub>.

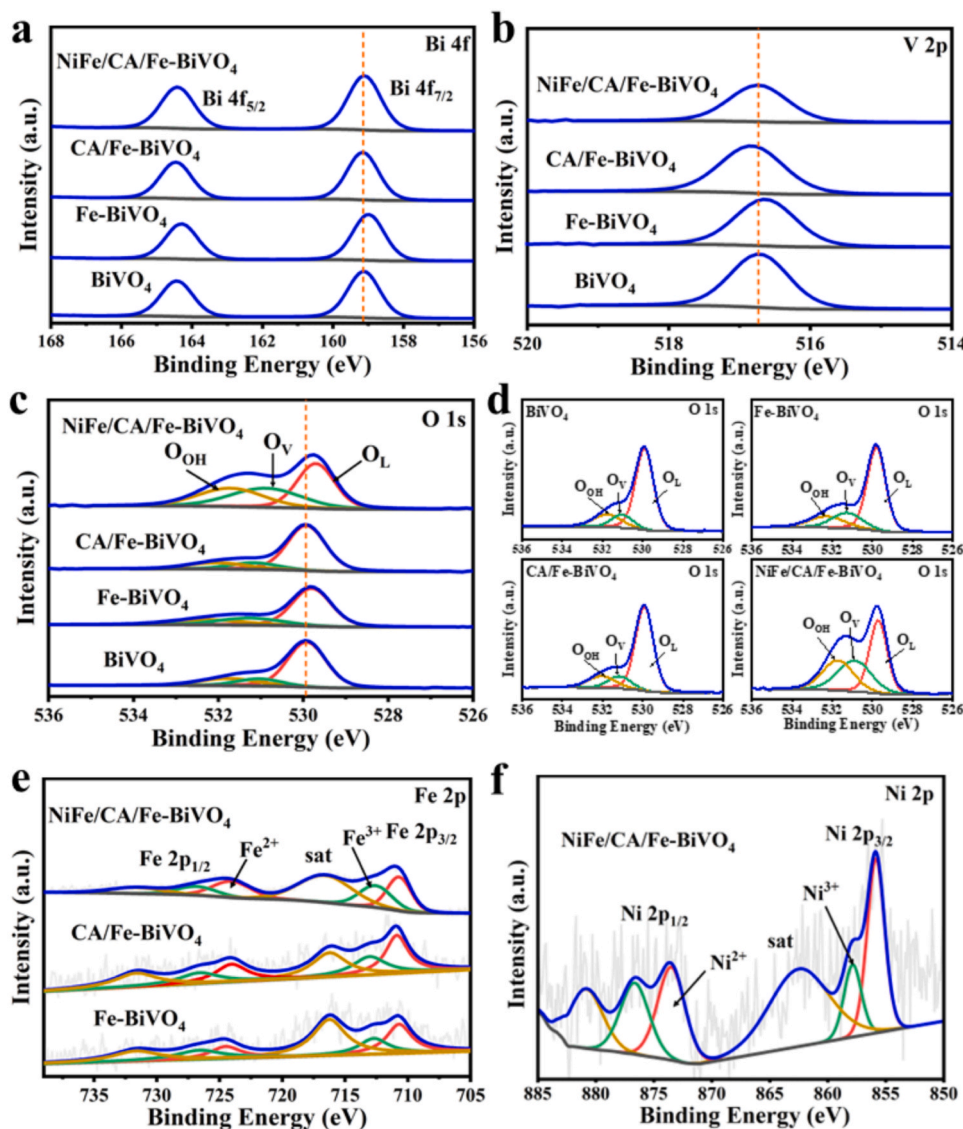


Fig. 7. XPS spectra. a) and b) Bi 4f and V 2p of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . c) and d) O 1s of  $\text{BiVO}_4$ ,  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . e) Fe 2p of  $\text{Fe-BiVO}_4$ ,  $\text{CA/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ . f) Ni 2p of  $\text{NiFe/CA/Fe-BiVO}_4$ .

attributed to  $\text{Ni}^{2+}$ , while the peaks of Ni 2p<sub>3/2</sub> (876.6 eV) and Ni 2p<sub>1/2</sub> (857.8 eV) are attributed to  $\text{Ni}^{3+}$  (Fig. 7f) [50,54]. After the reaction, the proportion increase of  $\text{Fe}^{3+}$  and  $\text{Ni}^{3+}$  (Fig. S13d and S13e) is due to the enrichment of surface holes (Fig. 5e) and the generation of superoxide intermediates (Fig. 6) during the reaction process. Meanwhile, the XPS peak positions of Bi 4f and V 2p (Fig. S13a and S13b) show nearly no changes. The amounts of  $\text{O}_\text{V}$  and  $\text{O}_\text{OH}$  significantly decrease after the reaction (Fig. S13c). XPS proves the proportion change of  $\text{Ni}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{O}_\text{V}$  of the  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode before and after the reaction. In addition, photocurrent density kept at mostly the initial value after the 12 h stability test at 0.8 V<sub>RHE</sub>. Based on XPS analysis and stability test, the co-catalyst underwent reconstruction during the reaction. The increase in the proportion of  $\text{Ni}^{3+}$  and  $\text{Fe}^{3+}$  enhance their chelating ability with oxygen in water molecules and are the catalytic active sites. Meanwhile, the reduced proportion of  $\text{O}_\text{V}$  improved the stability of the  $\text{NiFe/CA/Fe-BiVO}_4$  via regulating the electronic state of the co-catalyst surface.

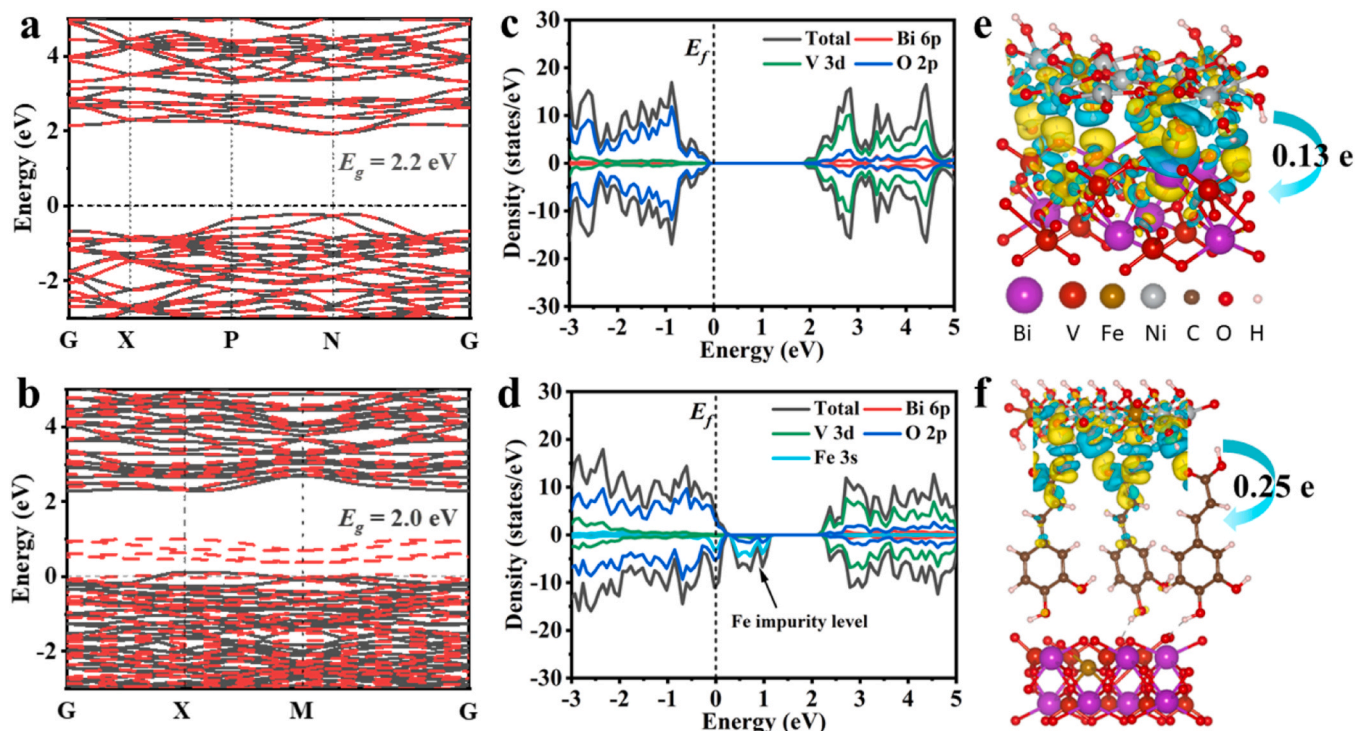
### 3.5. DFT calculation and analysis

Furthermore, the density functional theory (DFT) calculation has

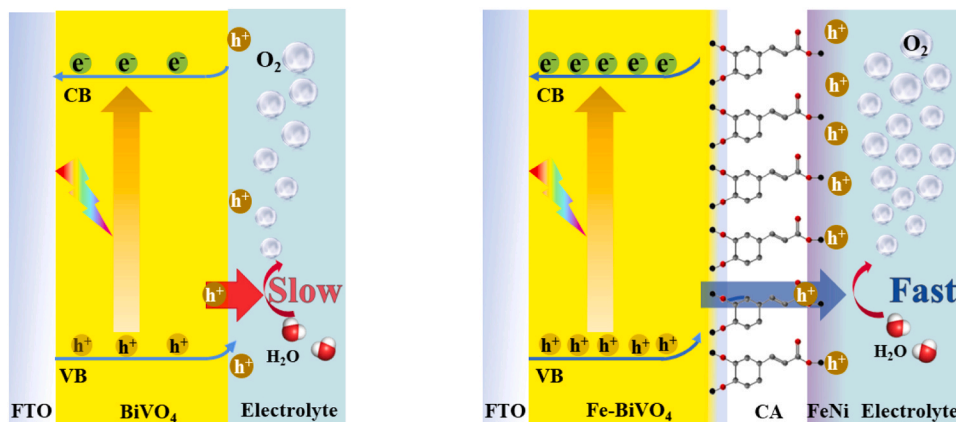
been utilized to reveal the changes of electronic states and charge transfer direction. Density of states (DOS) calculations were performed to illustrate the change in electronic states between  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ . Fe-doping generates the Fe impurity states and decreases the bandgap value of  $\text{BiVO}_4$  (Fig. 8a and 8b), which is the same as the experimental results. In addition, the replacement of Bi with Fe in  $\text{BiVO}_4$  bring about increased density of states near the VB maximum and CB minimum (Fig. 8c and 8d).

In order to clarify the charge transfer direction and separation, the charge density difference calculations were conducted for samples  $\text{NiFe/CA/Fe-BiVO}_4$  and  $\text{NiFe/BiVO}_4$ . Charge redistribution mainly occurred around the  $\text{NiFe/Fe-BiVO}_4$  interface and  $\text{NiFe/CA}$  interface, and hardly any change was observed in the inner  $\text{Fe-BiVO}_4$ . The change of charge density at the  $\text{NiFe/Fe-BiVO}_4$  and  $\text{NiFe/CA}$  interface showed that the electrons mainly transferred from NiFe to  $\text{Fe-BiVO}_4$  and  $\text{CA/BiVO}_4$  through the interfaces, respectively. Bader charge analysis demonstrates that NiFe co-catalyst donates 0.13 electron to  $\text{Fe-BiVO}_4$  for  $\text{NiFe/Fe-BiVO}_4$  (Fig. 8e). While for sample of  $\text{NiFe/CA/Fe-BiVO}_4$ , the number of 0.25 electrons are transferred from NiFe to  $\text{CA/Fe-BiVO}_4$  (Fig. 8f). The calculation results illustrate that CA facilitates electron transport from co-catalyst NiFe to  $\text{Fe-BiVO}_4$ , which enhances interfacial polarization,





**Fig. 8.** DFT calculation. a) and b) The calculated electron energy bands of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ . c) and d) DOS of  $\text{BiVO}_4$  and  $\text{Fe-BiVO}_4$ . e) and f) Charge density difference of  $\text{NiFe/Fe-BiVO}_4$  and  $\text{NiFe/CA/Fe-BiVO}_4$ .



**Fig. 9.** Schematic illustration of charge transfer and water oxidation of  $\text{NiFe/CA/Fe-BiVO}_4$  photoelectrode.

inter-interfacial coupling and electronic state modulation, thus effectively inhibiting the recombination of photogenerated carriers.

Based on the results mentioned above, the photoelectrochemical water oxidation and charge transfer of  $\text{NiFe/CA/Fe-BiVO}_4$  are illustrated in Fig. 9. Due to the strong interfacial interaction between the  $\text{Fe-BiVO}_4$  photoanode and the  $\text{NiFe}$  co-catalyst, photogenerated holes can rapidly migrate to the catalyst surface, while photogenerated electrons quickly transfer to the counter electrode through the external circuit, significantly facilitating charge separation and transfer. By anchoring the CA bridge connection layer, the surface states of  $\text{Fe-BiVO}_4$  are effectively passivated, controlling the electron states and enhancing the strong interfacial coupling between the  $\text{Fe-BiVO}_4$  and  $\text{NiFe}$  co-catalyst. Therefore, the recombination of photogenerated charge carriers is effectively suppressed and electron transfer from the  $\text{NiFe}$  co-catalyst layer to  $\text{Fe-BiVO}_4$  is efficiently promoted.

#### 4. Conclusion

In summary, we developed a novel photoanode synthesis method for PEC water oxidation through combination doping and co-catalyst strategy. First, uniform Fe doped  $\text{BiVO}_4$  was obtained by in-situ electrochemical doping and calcination. Subsequently, a hybrid  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode was fabricated by sequential deposition of caffeic acid (CA) as bridging reagent and  $\text{NiFeOOH}$  ( $\text{NiFe}$ ) as co-catalyst to  $\text{Fe-BiVO}_4$  through self-assembly. Under illumination with an applied bias of  $1.23 V_{\text{RHE}}$  (AM 1.5 G,  $100 \text{ mW/cm}^2$ ), the photocurrent density reached  $6.2 \text{ mA/cm}^2$ , accompanied with an ABPE of 2.15% at  $0.65 V_{\text{RHE}}$  for the PEC water oxidation reaction. Photoelectrochemical performance remained nearly the initial photocurrent density after 12 hours at  $0.8 V_{\text{RHE}}$ . Systematical characterizations revealed that the good PEC performance of the  $\text{NiFe/CA/Fe-BiVO}_4$  photoanode could be attributed to the simultaneous improvement in separation of photogenerated charge carriers and interfacial OER catalytic kinetics, which is resulted

from the synergetic effect between the Fe and Ni in the co-catalyst of NiFeOOH. In addition, EPR and in-situ FTIR confirm the generation of superoxide active species ( $O_2^-$  and  $\cdot O_2^-$ ) during the PEC water oxidation reaction. This work provides a new strategy for designing highly efficient composite photoanodes for PEC.

### CRediT authorship contribution statement

**Xiaohu Li:** Writing – original draft, Investigation, Formal analysis, Data curation. **Junhao Wu:** Software, Formal analysis. **Congzhao Dong:** Methodology, Investigation. **Yao Kou:** Data curation. **Chunlian Hu:** Validation, Formal analysis. **Jinnuo Zang:** Investigation. **Jiayu Zhu:** Methodology, Investigation. **Baochun Ma:** Resources. **Yuanyuan Li:** Resources, Software. **Yong Ding:** Writing – original draft, Supervision, Project administration, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data Availability

Data will be made available on request.

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### Supporting Information

Supplementary data associated with this article can be found in the online version.

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.124096](https://doi.org/10.1016/j.apcatb.2024.124096).

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